On the Analysis by Positive Rays of the Heavier Constituents of the Atmosphere; of the Gases in a Vessel in which Radium Chloride had been stored for 13 Years, and of the Gases given off by Deflagrated Metals.

By Sir J. J. Thomson, O.M., F.R.S.

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Sir James Dewar was kind enough to supply me with large quantities of the residues obtained from the evaporation of many thousand tons of liquid air. These residues had been absorbed by charcoal which had been kept in a sealed vessel. I have analysed these residues by the Positive Ray Method. The general arrangements were the same as those described in my book on Positive Rays. Some alterations, however, were necessary, as I used for these investigations a much more powerful induction coil than the one I had hitherto employed. With this coil so much heat was developed in the part of the tube near the cathode that any wax joints in that neighbourhood, even though they were cooled by a water jacket, gave off enough gas to spoil the vacuum for positive ray purposes. To avoid this difficulty I substituted for the wax joint, which formed the connection between the glass bulb in which the discharge takes place and the brass vessel which contains the camera, a joint made by a method used by Mr. Roebuck, and described by him in the 'Physical Review,' vol. 28, p. 264 (1909). The method consists in first making on the outside of the glass tube a deposit of platinum by one or other of the devices used for platinising glass, and then depositing slowly by electrolysis a layer of copper on the platinum. With care this layer can be made thick and firm enough to enable a brass tube connected with the camera vessel to be soldered on to it, and an air-tight joint obtained which does not give off gas when heated by the discharge.

The method adopted to analyse the gas was to put some of the charcoal containing the gaseous residues into a small vessel A, which was fused on to the discharge tube B; there was a tap between A and B, and this was turned until B had been exhausted to a very low pressure; there was also a very fine capillary tube in the circuit between A and B, and when the pump used for exhausting the discharge tube was kept in action a continuous stream of gas from A could be kept flowing through the discharge tube without making the pressure too high to obtain good photographs. Just before the tap between A and B was opened a photograph was taken with ordinary air going through the discharge tube, and the lines in this were compared with those on the photograph obtained when the gas from A was flowing through the tube.

As the charcoal was found to have absorbed large quantities of water vapour, it was necessary to have a phosphorus pentoxide in connection with A for several days before a photograph was taken, otherwise so much water vapour came out of the charcoal that the pressure in the discharge tube got so high that sharp photographs could not be taken. The charcoal also contained a considerable amount of mercury vapour. The bulb A was placed in a bath and photographs were taken with A at the temperature of the room, at 100° C., and at the highest temperature the bulb would stand without softening. The difference in the photographs at different temperatures consisted in variations in the intensity of the lines rather than in the absence or presence of new lines. The most striking characteristic of the photographs obtained with the residual gas was the predominance of the xenon line over all the lines due to the other inert gases. The xenon line was very strong, but in the first few photographs I could not detect either the krypton or the neon lines. As, however, the inert gases get absorbed by the electrodes to a very remarkable extent, they tend to accumulate in the electrode after the discharge has been maintained for a long time, and after about 20 photographs had been taken I could just detect the krypton line; it never, however, was otherwise than exceedingly faint, and the quantity of krypton in the residual gas must be very small indeed compared with that of the xenon. I was never able to detect the neon line. The evaporation of the gases from the charcoal seems to have effected a fractionation, with the result that there is a great excess of the heavier gas in the fraction retained by the charcoal.

In addition to the xenon line there were two faint lines of great interest, both indicating gases of greater atomic weight than xenon. The stronger of the two lines has a value of m/e equal to 163 ± 5, the weaker has $m/e = 260 \pm 10$. The lines are so faint that it is difficult to get very accurate measurements. A great deal, however, can be done in the measurement of faint lines by a proper choice of the intensity of the illumination. These lines are very difficult to see in a strong light, but when the intensity of the illumination is reduced they may become quite distinct and measurable. It is convenient to measure these lines in a room where the illumination varies considerably from place to place, and to move about until the most favourable place for good seeing is found.

Origin of the Lines 163 *and* 260.

These lines might, as far as their atomic weights go, originate from molecules of krypton and xenon respectively, and I am inclined to think that this is the correct interpretation, there are, however, many properties of these lines which seem at first sight to be incompatible with this explanation. For example the line 163 frequently occurs on photographs when the line due to krypton itself cannot be detected, again I have positive ray photographs, taken when the gas in the discharge tube was rich in krypton, where the krypton line is very strong, but which do not show any trace of the line 163. This objection would be fatal were it not for the way in which the residual gases we are considering had been collected and stored. Let us assume for a moment that molecules of krypton can exist, but that when krypton is in the gaseous state the molecules are few compared with the atoms; let us now suppose that this mixture is absorbed by cold charcoal and then allowed to evaporate slowly. Since the Kr molecules are more complex than the atoms they will probably be much more firmly held by the charcoal so that the atoms will evaporate much more rapidly than the molecules, thus the residue in the charcoal will get richer and richer in molecules as compared with atoms. In fact we may suppose that the explanation which we gave to explain why the residual gas was much richer in Xe than in Kr, though there is more krypton than xenon in the atmosphere, can be extended to explain why, though the Kr molecules in the atmosphere are few compared with the atoms, they are in the majority in the residues.

As molecular krypton would be heavier than atomic xenon it would probably not come out of cooled charcoal any more readily, if so readily as xenon. Thus the ordinary method of separating krypton from xenon would separate the atomic but not the molecular form of this gas. Thus xenon obtained in this way would contain some krypton which, when a spark was passed through the mixture, might give rise to the krypton spectrum. Professor Moore has prepared xenon which does not show the krypton spectrum. It must be remembered, however, that the positive ray photographs indicate that the quantity of the substance giving the line 163 in the atmosphere is an exceedingly small fraction of the amount of xenon, and in some mixtures of two gases the spectrum of one of the constituents is not excited unless more than a certain percentage of it is present in the mixture.

There is one important respect in which the substance giving the line 163 shows the characteristics of an atom rather than those of a molecule, for on two or three of the strongest photographs it can be seen that this line is prolonged towards the axis, which indicates that the source of this line can carry a double charge of electricity. A double charge of electricity is in the great majority of cases confined to atoms, though there are a few instances known where the molecule of a compound carries a double charge.

The strongest argument in support of the view that this line is due to a molecule of krypton, and not a new element, is that such an element would not fit in well with the periodic law. It is perhaps possible to lay too much stress on this argument, for the atomic weight would indicate that the element would be in the parts of the table covered by the rare earths, a region where there seems to be great confusion.

The existence of molecules of inert gases is of considerable interest. I have shown from the evidence given by positive ray photographs that charged molecules of helium occur in the discharge tube. We do not know, however, whether such molecules could exist without a charge. If the line 163 is due to a molecule of krypton, this molecule must be stable when uncharged. The existence of molecular krypton would indicate that this element, like some others, could show two valencies, the normal zero valency and another. If this is so we might expect krypton to combine with some of the other elements to form compounds. Such a compound may be the origin of another line, which I have observed in the positive ray spectrum of the gas supplied to me by Sir James Dewar; this line corresponds to an atomic weight of about 118; it is not like the lines 160 and 260 found on all the plates, but only on a few of them; when it does occur, however, it is stronger than either of these lines. I have never been able to get the line 260 sufficiently intense to feel sure that I could see a prolongation if there was one.

From these experiments we conclude that the atmosphere contains small quantities of two constituents heavier than xenon. As the molecular weights of these are about twice the atomic weights of krypton and xenon it seems probable that these heavier constituents are molecules of krypton and xenon. The lighter of the two constituents is more abundant than the heavier, but the amount of either is only a very small fraction of that of xenon.

I made experiments to see if these constituents showed any properties analogous to those of the emanations of radio-active substances. If such emanations are placed in a closed vessel they increase the ionization in the vessel and consequently the rate of leak of a charged insulated body placed inside the vessel. I could not, however, detect any change of leak when the gases which had been absorbed by the charcoal were introduced into an ionization vessel.

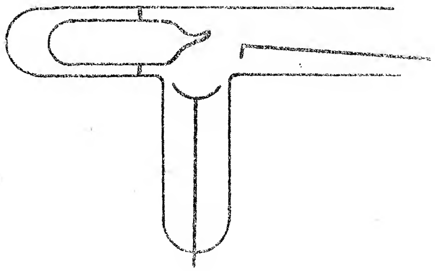
Gases Obtained from a Tube which had Contained Radium for Thirteen Years.

The Royal Society were kind enough to allow me to have the use of the 70 mgrm. of $RaCl_2$ which had been used by Sir T. E. Thorpe in his determination of the atomic weight of radium, and by Sir James Dewar in his experiments on the amount of helium given off by radium. The radium had been sealed up in a glass tube from which the air had been exhausted by Sir James Dewar in 1909.

To analyse the gases in this tube I found it necessary to construct a new positive ray apparatus, as the one that had been used for the preceding experiments had got so contaminated with xenon that I was unable, either by repeated sparking or by passing continuous currents of air through the tube, to get rid of indications of the xenon line on the photographs.

The operation of transferring the gases from inside the sealed radium tube to the discharge tube without introducing other gases presented considerable difficulty; a very satisfactory solution was obtained by using the following method.

The radium tube was placed in a vessel A, which was connected with the discharge tube B by a circuit containing a tap and fine capillary tubes for regulating the rate of flow from the gas in A through B. A side tube was attached to A and in this there was a concave electrode which, when it was used as a cathode, caused a beam of cathode rays to focus on the tube containing the radium, the impact of these rays bored a small hole through the radium tube through which the gases from this tube could pass into the discharge tube. The adjustment for the right position of the radium tube and the concave cathode was made by taking a dummy tube of the same size and shape, and as nearly as could be judged of the same thickness as the radium tube. When this had been adjusted so that a hole was invariably pierced through the tube when the cathode rays were turned on, the dummy was replaced by the radium tube, and this was successfully pierced by the cathode rays. I had expected that owing to the long exposure to the radium the glass would be likely to explode when it was fractured, and precautions were taken



to prevent any loss of radium or fracture of the tube A should this happen. Nothing of the kind however occurred, and there was not even a trace of a crack round the hole.

It should be mentioned that before the cathode rays were turned on, the discharge tube and the vessel A were exhausted to a high vacuum by a Gaede pump and cooled charcoal. A photograph was taken just before the radium tube was pierced and another immediately after. On examining the photograph taken after the gas from the radium had got into the discharge tube it was found, as might be expected, that it showed a very strong helium line; the only other line which was not on the plate taken just before the radium tube was pierced was a very faint line for which $m/e = 5$. I could not see either the neon line or that corresponding to H_3. The lines due to the atom and molecule of hydrogen were very strong on both photographs. It must be remembered that the tube in which the radium was contained had been exhausted before sealing so that the α-particles from the radium had nothing to bombard except the walls of the tube and the radium chloride itself.

I have opened at one time or another several tubes which have contained radium for considerable periods though none for so long as the one now under consideration. These showed the "3" line and some of them the neon line. It must be remembered, however, that these tubes had not, like the present one, been highly exhausted, but were full of air at atmospheric pressure. I did not observe the "5" line on the older photographs, but these were not nearly so sharp and distinct as those taken with the present tube.

As the "5" line appears on photographs which do not show any trace of lines corresponding to $m/e = 10$ or 20, it is not likely to be due to a doubly charged atom; a molecule containing one atom of helium and one of hydrogen would give a line for which $m/e = 5$, and considering that in the radium tube there is both helium and hydrogen, and that these have been exposed to the action of α-rays, it is, I think, probable that the line is due to this compound.

After all the gas which had come out of the radium tube had been utilised for taking photographs, the bulb A was filled with air which was left for several days standing over the radium, then some of this gas was put into the discharge tube and positive ray photographs taken. One of the features of these photographs was the intensity of the lines corresponding to the doubly charged atoms of oxygen, nitrogen, and carbon. These lines are always found in good photographs of air, even though it has not stood over radium; but the radium seems to produce a considerable increase in their intensity. It is not, however, the only agent that does so, for I have found that the gases given off when very fine metallic wires are deflagrated by powerful electric currents also give rise to photographs in which the lines due to these doubly charged atoms are very much enhanced in intensity. I have succeeded in obtaining photographs on which these lines are as strong as any on the plate.

The study of these enhanced lines has brought out many interesting features which were not detected with the fainter lines of the earlier photographs. One of the most important of these is that the lines due to the doubly charged atoms, like those due to the simply charged ones, show prolongations towards the vertical axis. If d is the normal minimum distance from the vertical axis, *i.e.*, d is the minimum electrostatic displacement of a singly charged atom, then it was found that on many of the plates the lines due to the doubly charged atoms of oxygen, nitrogen, and carbon were prolonged, so that the minimum electrostatic displacement was only $2d/3$. On a few of the best plates the lines corresponding to the doubly charged oxygen and nitrogen atoms were prolonged until the minimum electrostatic displacement was only $d/2$. I could not be sure that the prolongation of the line due to the carbon atom was as great as this. The prolongation beyond the normal stopping-place indicates* that some of the carriers had while in the discharge tube a greater charge, and so by falling through the same potential difference acquired greater energy than the normally charged atom. They lost the extra charge after leaving the discharge tube and before being photographed, so that the value of m/e for the prolongation is the same as for the main portion of the curve.

The energy possessed by a carrier is inversely proportional to its displacement by the electrostatic field, and since the energy is proportional to the charge carried by the particle in the discharge tube, this charge will be inversely proportional to the minimum distance of the parabola from the vertical.

Thus, if a parabola has a prolongation such that the minimum distance of a point from the vertical is $d/2$, while d is the normal minimum distance, it shows that the carrier which gives rise to the parabola can occur in the discharge tube with twice the normal charge. If the prolongation only extends to $2d/3$ it shows that the carrier can occur in the discharge tube with a charge $3/2$ times the normal charge. By the normal charge we mean the charge carried by the particles while they are passing through the electric and magnetic fields. Now in the lines corresponding to the doubly charged atoms of oxygen, nitrogen and carbon, the normal charge is two units, hence, since these show a prolongation extending to $2/3$, some of these atoms must have had in the discharge tube a charge equal to $(3/2) \times 2$ or 3 units. While since the lines due to oxygen and nitrogen show a prolongation to $d/2$, some of these atoms must have had in the discharge tube a charge equal to 2×2, *i.e.*, 4 units. If some of the atoms retained their triple charge while passing through the electric and magnetic fields we should have parabolas for which m/e was for oxygen, nitrogen, and carbon 16/3, 14/3, 12/3 respectively. I have plates on which the first two of these are quite visible. If the atoms retained their quadruple charges there would be parabolas for which $m/e = 16/4$, $14/4$ for the oxygen and nitrogen atom respectively; these parabolas are, however, so faint that I have not been able to detect them. The amount of prolongation of the parabolas corresponding to the doubly charged atoms shows, however, that atoms with four-fold charges must exist.

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* See 'Rays of Positive Electricity,' 2nd edition, p. 77.

This result has an important bearing on the question of the number of electrons in the outer layers of the atoms of carbon, nitrogen and oxygen. For since each unit of positive charge involves the removal of an electron from the outer layer of the atom, and since atoms of oxygen and nitrogen with four charges and atoms of carbon with three have been detected by the positive rays, the atoms of oxygen and nitrogen cannot have less than four electrons in the outer layer, nor can the atom of carbon have less than three. These results are thus in accordance with the view that the atom of oxygen has six, the atom of nitrogen five, and the atom of carbon four electrons in the outer layer.

A very interesting line, for which $m/e = 10$, was first detected on some plates on which the lines due to the doubly charged atoms were exceptionally well developed. When attention had once been called to its existence, closer scrutiny of the earlier plates showed that a faint line in this position is by no means uncommon. When neon is in the tube a line corresponding to $m/e = 10$ is generally found, but this is always accompanied by a much stronger one for which $m/e = 20$.

The peculiarity of the line we are now considering is that it occurs when there is no trace of a line for which $m/e = 20$, and when there is no reason for suspecting the presence of neon. If the line is due to a singly charged atom it involves the existence of a new element; on the other hand, if it is due to a doubly charged one we have to explain the absence of the line due to the singly charged atom. An explanation which surmounts these difficulties is that the line is due to a doubly charged oxygen atom combined with four atoms of hydrogen. A doubly charged oxygen atom has lost two electrons and thus has four left in the outer layer, the same number as are in an uncharged atom of carbon. The valency of the doubly charged oxygen atom will thus be the same as that of carbon, so that it can form the compound $O_{-\,-}H_4$; the value of m/e for this is 10. As the existence of this compound depends on the double charge on the oxygen atom it could not exist with a single charge, hence the absence of the line $m/e = 20$. The singly charged oxygen atom would have five electrons in the outer layer and would therefore have the same valency as the neutral nitrogen atom, it could form the compound $O-H_3$. The value of m/e for this is 19, and a line with this value of m/e is one of the lines which occur most frequently on photographs of the positive rays.

Gases given off when Metallic Wires are Deflagrated.

It has recently been asserted that helium is given off in considerable quantities when thin metallic wires are deflagrated by powerful electric currents. Some time ago I found that small quantities of helium were given out by many substances when bombarded by cathode rays; the quantity was very small and the emission ceased after the bombardment had lasted for some time. I could not detect any helium if the substance were merely heated without bombardment by cathode rays. I have recently tested by the Positive Ray Method the gases given off when fine wires of tungsten, gold, or copper are deflagrated by powerful electric currents. I could not detect any helium, the H_3 line was however quite strong. This is in agreement with my earlier experiments when I found I could get H_3 but not He by heating without bombardment.

Summary.

The paper contains an account of applications of the Positive Ray Method of Analysis to several problems. The first is that of the heavier constituents of the atmosphere. It is shown that at least two constituents heavier than xenon are present in the atmosphere. The approximate values of the atomic weights are 163 and 260; the lighter of these is the more abundant, but the quantity of it in the air is very small compared with that of xenon.

The source of these lines is discussed; on the whole, it seems most probable that they are due to molecules of krypton and xenon.

These gases were observed in the residues of large quantities of liquid air which were very kindly placed at my disposal by Sir James Dewar.

The second application was to the analysis of the gases in the sealed tube in which the radium chloride belonging to the Royal Society had been sealed for thirteen years; the tube had been exhausted by Sir James Dewar before sealing. In the photographs obtained with this gas the helium line was very strong; there was no neon, there was however a faint line for which $m/e = 5$, due probably to a compound of helium and hydrogen.

The analysis was also applied to gases which had stood over radium and also to the gases lit by deflagrating wires. From the study of the photographs obtained with these gases, quadruply charged atoms of oxygen and nitrogen

were detected and triply charged atoms of oxygen, nitrogen, and carbon. The compound OH_4 was also detected carrying invariably a double charge.

I am much indebted to the Royal Society for the loan of the radium; to Sir James Dewar for placing at my disposal large supplies of the residues of liquid air, and to Mr. E. Everett for the assistance he has given me in making the experiments.

On the Scattering of β-particles.

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§ 1. *Introduction.*

An account has recently been published* by Dr. J. A. Crowther and the writer, of some experiments on the scattering of β-rays by thin sheets of matter. The angles of deflection investigated ranged from 4° to 8°. The main results obtained may be summarised as follows:—

(1) The scattering observed was "single," *i.e.*, due to one collision with an atomic nucleus.

(2) The law of force governing such collisions appeared to be that of the inverse square.

(3) The single scattering theory due to Sir Ernest Rutherford requires the scattering power of an element to be proportional to the square of its nuclear charge. This relation was found to hold only in the case of the elements carbon and aluminium, if the nuclear charge consist of as many positive units as the atomic number of the element.

(4) For the elements copper, silver, gold and platinum, a comparison with previous results extending the range of the deflection angle to 20°† showed that a rapid increase in the scattering power of these elements appeared to take place as the thickness and angle of deflection were increased.

The experiments to be described were instituted to test the truth of (4) and to confirm the other conclusions under the somewhat easier experimental conditions prevailing at larger angles of deflection. They were carried out at from 12° to 25°.

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* Crowther and Schonland, 'Roy. Soc. Proc.,' A, vol. 100 (1922).

† Crowther, 'Roy. Soc. Proc.,' A, vol. 84 (1910).